[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, POLYTECHNIC INSTITUTE OF BROOKLYN]

Photoreduction of Metal Ions by Visible Light[1]

BY GISELA K. OSTER AND GERALD OSTER

RECEIVED APRIL 14, 1959

The photoreduction of a variety of metal ions (Fe^{3+}, Ti^{4+}, Cu^{2+}, $CrO_4^=$, Ag^+, $MoO_4^=$, Hg^{2+}) can be effected with visible light using certain dyes as sensitizers. The reaction is carried out in the presence of chelating agents which serve as electron donors for the light-excited dye but are not reducing agents for the metal ions. Only dyes which are photoreducible are sensitizers for the reduction of the metal ions. The photoreduced dye serves as the reducing agent for the metal ion and is thereby regenerated. As a consequence, the photobleaching of the dye exhibits an induction period proportional to the metal ion concentration and only starts to fade after all the metal ions are reduced. Quantitative studies were carried out with ferric ion using methylene blue as the sensitizer and ethylenediaminetetraacetic acid as the electron donor. The ferrous ion produced was complexed with *o*-phenanthroline. A gel which was crosslinked with mercuric ion and contained dye and electron donor collapses on illumination with visible light. Conversely, gelatin containing bichromate ion, dye and electron donor is crosslinked on illumination with visible light.

Introduction

The photoreduction of ferric salts and of bichromates by ultraviolet light has been known for more than a century.[2] Ultraviolet photoreductions involve the direct excitation of a metal ion complex and reduction is believed to take place by an electron transfer process from the excited metal on to its ligand.[3,4] We have found that a wide variety of metal ions can be photoreduced by means of visible light using certain dyes as sensitizers. In the visible light reduction the dye is the light excited species and, as will be shown, is reduced; the reduced dye, in turn, reduces the metal ion and reverts to the normal form of the dye. The source of electrons is a chelating agent containing secondary or tertiary nitrogens (excluding aromatic heterocyclics) which acts as a reducing agent for the light excited dye[5] but is not a reducing agent for the metal ion.

By means of dye-sensitized photoreduction, those systems whose properties depend upon the valence state of a metal ion can be rendered sensitive to and controllable by visible light. Examples of such phenomena are demonstrated in the present paper by dye-sensitized photocrosslinking and photodegradation of certain high polymers where the macromolecules are connected by metal ions.

Experimental

Materials.—The dyes used were Histological Grade made by National Aniline and sold by Fisher. Chelating agents were Analytical Grade obtained from Dow and from Eastman. All metal salts (excluding titanium lactate from Du Pont) were Fisher Analytical Grade. Polyacrylamide (type 75) was obtained from American Cyanamid. Gelatin, pigskin highest purity, was obtained from Eastman.

Procedure.—In all cases a 500-watt TDC tungsten lamp slide projector 20 cm. from the sample was employed. The solutions were illuminated with white light where light below 400 mμ was removed with a Corning type 3-73 glass filter. The light transmitted was rendered monochromatic by interposing appropriate interference filters (Bausch and Lomb) between the sample and the photomultiplier tube (RCA 1P22) of an Aminco photometer unit. Changes in transmission were recorded on a Leeds and Northrup Speedomax type G recorder.

For qualitative observations we employed typically a solution of the following concentrations: 10^{-4} *M* in dye, 10^{-3} *M* in metal ion, and 10^{-2} *M* in chelating agent. The experiment was carried out so that the reduced metal ion species would always appear in a colored form different from that of the original solution. Thus the formation of ferrous ion is observed by its red colored complex with *o*-phenanthroline. In these experiments 20 ml. of solution in a 1 cm. path length 5 × 5 cm. flat cell having provisions for deaerating with prepurified nitrogen are illuminated with white light. The formation of the colored reduced metal species and the disappearance of the dye were followed continuously.

For the crosslinking and degradation studies films containing polymer (10% by weight), dye, metal ion and chelating agent were cast on microscope slides and illuminated through a photographic negative. In the case of the photosensitized crosslinking systems, the unexposed portions wash away with water and the exposed portions remain behind as a sharp raised image. Conversely, in the case of photosensitized degradation of metal complexed gels, the unexposed portions are insoluble in water while the exposed portions dissolve away.

Results

Methylene blue is photoreduced to the leuco form in the presence of ethylenediaminetetraacetic acid (EDTA) (curve I of Fig. 1). If ferric ion is present there is an induction period during which the dye is not faded and after which fading then proceeds (curves II and III of Fig. 1). During the induction period ferrous ion is being produced as evidenced by the formation of the red complex of ferrous ion with *o*-phenanthroline (Fig. 2). For low ferric ion concentrations the induction period is proportional to ferric ion concentration, but under conditions of our experiment the curve shows a positive deviation from linearity at high ferric ion concentrations (Fig. 3). This deviation is of purely photometric origin and arises from the fact that the absorption spectrum of *o*-phenanthroline–ferrous complex overlaps with the methylene blue spectrum. Hence the red complex acts as an internal filter for the blue dye. This filtering action is also responsible for the somewhat lower apparent rate of fading of methylene blue after the induction period (Fig. 1). By the simple expedient of introducing before a dye–EDTA solution a cell containing red complex of the same concentration as that of an illuminated sample, one can demonstrate that the lowered rate of fading was due to the filtering action of the red complex.

Large amounts of ferric ion can be reduced by dye sensitization. For example, in one experiment a fifty-fold excess of ferric chloride over dye en-

---

[1] Presented at the 135th National Meeting of the American Chemical Society, Boston, April 9, 1959.

[2] J. Plotnikow, "Allgemeine Photochemie," 2nd Ed., Walter de Gruyter Co., Berlin, 1936, Part 4, Sec. II.

[3] E. Rabinowitch, *Rev. Mod. Phys.*, **14**, 112 (1942); G. K. Rollefson and M. Burton, "Photochemistry," Prentice-Hall, Inc., New York, N. Y., 1946, Chapter 14.

[4] M. G. Evans and N. Uri, *Symp. Soc. Exp. Biol. No.* 5, p. 130 (1951).

[5] G. Oster and N. Wotherspoon, THIS JOURNAL, **79**, 4836 (1957).

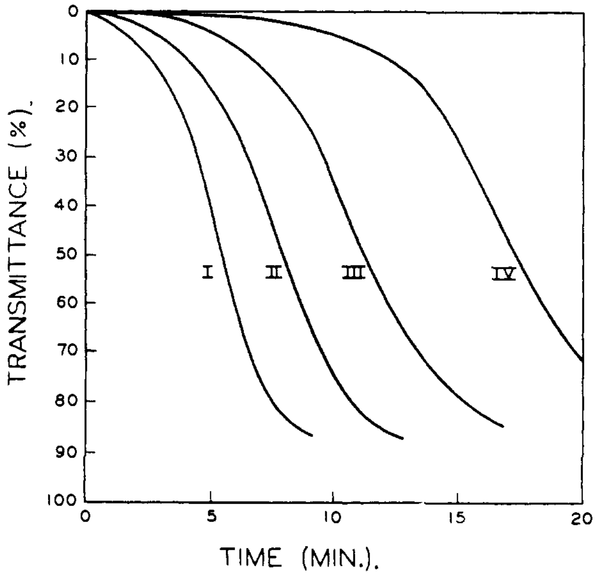

Fig. 1.—Photobleaching of methylene blue: transmission at 630 mμ; dye concentration 5×10^{-5} M, EDTA concentration 1×10^{-3} M, *o*-phenanthroline concentration, 4×10^{-3} M, FeCl$_3$ concentrations: I 0, II 0.5×10^{-4} M, III 1×10^{-4} M, IV 2×10^{-4} M; all in 0.01 M acetate buffer at *p*H 5.0.

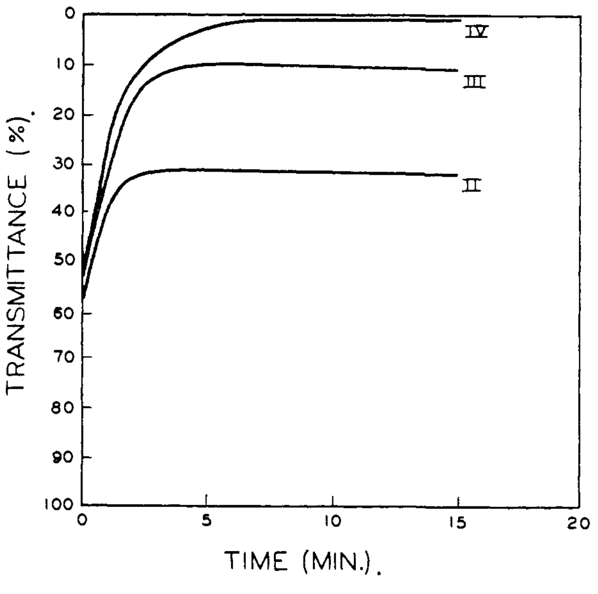

Fig. 2.—Production of ferrous ion (complexed with *o*-phenanthroline): transmission at 518 mμ; concentrations as in Fig. 1.

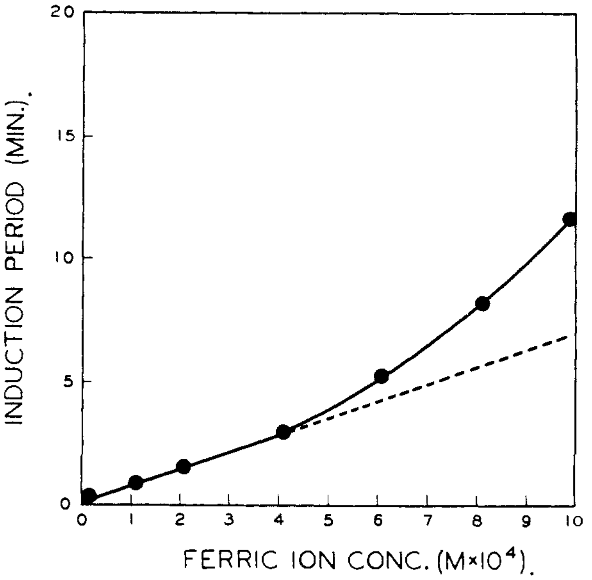

Fig. 3.—Apparent induction period for the photobleaching of methylene blue: dye concentration 5×10^{-5} M, EDTA concentration 1×10^{-2} M, *o*-phenanthroline concentration 4×10^{-3} M, in 0.01 M acetate buffer at *p*H 5.0.

abled the complete reduction of the metal ion. The fact that complete reduction of the ferric ion to ferrous ion (complexed with *o*-phenanthroline) takes place is shown by a quantitative comparison of the transmission of the red complex with the known molecular extinction coefficient (namely, 1×10^4 at 518 mμ) of the complex.

The reactions described above were carried out at *p*H 5 in order to ensure that no autoxidation of ferrous ion occurs even if trace amounts of oxygen were inadvertently present in the solution. At *p*H 5 the ferrous-*o*-phenanthroline complex is stable both with respect to oxygen and with respect to EDTA. Furthermore the complex does not serve as a reducing agent for light excited dye. The dependence of the rate of production of the ferrous complex upon EDTA concentration is the same as the dependence of the rate of fading of methylene blue upon EDTA, ferric salt being absent. At *p*H 5 the rate of fading of methylene blue at a concentration of 10^{-5} M in dye and 10^{-2} M in EDTA has a quantum yield of 0.0015. At higher *p*H values the photobleaching is much more rapid,[5] but then ferrous ion is too readily oxidized.

In order to take into account any possible direct photoreduction of ferric ion by the blue component of the white light employed, we irradiated a solution of ferric chloride at *p*H 5 containing *o*-phenanthroline but not containing dye. No photoreduction was observed under these conditions. If, however, EDTA is present, the red ferrous complex appears, but the rate of its formation is only 3% of the rate one observes when dye is present. Consequently, direct photoreduction processes of ferric ion are of no appreciable consequence in the present studies.

Calcium ion retards the photoreduction of ferric ions. Thus if CaCl$_2$ is added to equal the concentration of EDTA, the rate of ferrous production is approximately one-tenth that of the solutions not containing calcium ion. Increasing the ratio of calcium ion to EDTA even to a value of 10 does not give a rate of ferrous production differing much from that for a ratio of unity.

Since the ferrous complex absorbs over a broad portion of the middle of the visible spectrum, we were limited to only blue or to yellow dyes as sensitizers for the ferric chloride reduction. Proflavine, a yellow acridine dye, is a very effective sensitizer for the photoreduction of ferric chloride and shows the same qualitative effects of induction period as does methylene blue.

A number of qualitative dye-sensitized photoreductions were carried out using proflavine at a concentration 10^{-5} *M* and triethanolamine at a concentration of 10^{-2} *M* which had been adjusted to *p*H 7.0 with HCl. On illumination with white or blue light one observes that: (1) ferric ion is reduced to ferrous ion as shown by the formation of the red *o*-phenanthroline complex; (2) titanic ion (in the form of the lactate) is reduced to titanous ion as shown by the production of a purple coloration; (3) cupric ion (as the sulfate) is reduced to cuprous ion as shown by the formation of red cuprous oxide; (4) hexavalent chromium (as bichromate ion) is reduced to trivalent chromium as shown by the formation of a green color; (5) silver ion (as the nitrate) is reduced to metallic silver as shown by the formation of a mirror; (6) hexavalent molybdenum (in the form of the molybdate ion) is reduced successively to the pentavalent, tetravalent and trivalent states as shown by the color changes in the sequence colorless, blue, green and brown; (7) mercuric ion (in the form of the chloride) is reduced to the monovalent and metallic forms as shown by the appearance of a white to grey precipitate.

Other dyes were tested for their action as sensitizers. Fluorescein and its halogenated derivatives (eosin, erythrosin, etc.) were effective as were all the thiazines (methylene blue, azure A, etc.). Of the acridines only the 3,6-diaminoacridines were effective. No azo or azine dye was effective as a sensitizer.

We found that mercuric ion will convert a basic solution of polyacrylamide into a clear gel which is not swollen appreciably by water. Neutralized triethanolamine was added to the extent of 0.5% to a 10% aqueous solution of polyacrylamide containing 0.01% mercuric chloride and the system was gelled by exposing to ammonia vapors. This gel when containing any of the aforementioned dyes to the extent of 0.001% collapses, *i.e.*, it liquefies, when exposed to visible light. The gel collapses in the dark if strong reducing agent (*e.g.*, sodium hydrosulfite) is added. The reverse effect occurs with the gelatin bichromate system sensitized with dye. Here 5% gelatin containing 5% potassium bichromate, 0.05% neutralized triethanolamine and any one of the aforementioned dyes is rendered water-insoluble when exposed to visible light.

Discussion

Photoreduced dyes are strong reducing agents and can reduce various inorganic and organic substances. The leuco form of the dye may have a reduction potential as much as −1.2 volt, as is the case with proflavine.[6,7] Certain dyes in the presence of mild reducing agents which are incapable of reducing the dye in the dark, are reduced to their leuco forms when illuminated. Energy is derived from the light to produce the powerful reducing agent. Our results show that only those dyes which are known to be photoreducible[5,8-10] can serve as sensitizers for the visible light photoreduction of metal ions.

Since photobleaching of methylene blue does not take place as long as ferric ion is present and since during this induction period ferrous ion is produced, it is clear, therefore, that the photoreduced dye serves as the reducing agent for ferric ion and is thereby reoxidized to the colored form of the dye. This oxidation of the leuco dye by ferric ion is practically instantaneous since one obtains an inhibition of fading rather than a mere retardation. The continuous photoreduction of dye and its regeneration by ferric ion takes place until all the ferric ion is consumed.

The rate-determining step in the dye sensitized photoreduction of metal ions is the photoreduction of the dye. This is evident from the fact that the rate of reduction of metal ions has the same dependence on *p*H and on reducing agent concentration as does the photoreduction of the dye in the absence of metal ions. The rate of photoreduction of the dye after ferric ion is consumed is the same as the rate of photoreduction of the dye in the complete absence of metal ions, taking into account, of course, the photometric corrections discussed under Results.

Any mild reducing agent can serve as the electron donor in the photoreduction of dyes. However, it is sometimes difficult to find a reducing agent which will not reduce the metal ion directly. This difficulty is circumvented by employing the chelating agents which serve as electron donors for the light excited dyes. These compounds will not reduce metal ions. It is not understood why they act as reducing agents for excited (actually triplet state) dyes. We employed an excess of chelating agent over metal ion concentration since the chelate–metal complex does not serve as an electron donor for the light excited dye. This is clearly shown by the retardation effect of calcium ion. Incidentally, by studying the effect of ions on the rate of photoreduction of dye in the presence of EDTA one can determine quantitatively the amount of ion present.[11]

The dye sensitized photodegelling of acrylamide complexed with mercuric ion is due to a reduction of the mercuric ion which in its reduced form is unable to crosslink the polymer. Similarly the insolubilization of gelatin in the dye-sensitized bichromate reaction is due to reduction of the chromate ion since reduced chromium (probably as a hydrate of Cr^{3+}) is known to crosslink gelatin.[12]

BROOKLYN, NEW YORK

---

(6) B. Breyer, G. S. Buchanan and H. Duewell, *J. Chem. Soc.*, 360 (1944) (polarographic half-wave potential).

(7) G. Oster and E. Schatz, ACS 135th National Meeting, Boston, April 1959 (photovoltaic effect).

(8) A. H. Adelman and G. Oster, THIS JOURNAL, **78**, 3977 (1956).

(9) F. Millich and G. Oster, *ibid.*, **81**, 1357 (1959).

(10) G. Oster, J. S. Bellin, R. W. Kimball and M. E. Schrader, *ibid.*, **81**, 5095 (1959).

(11) J. Joussot-Dubien and G. Oster, to be published.

(12) See, for example, K. H. Gustavson, *Advances in Protein Chem.* **5**, 354 (1949).